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"THE IMPURITY RELATED STUDIES OF HIGH T_C SUPERCONDUCTING MATERIALS"

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A-1

Impurity Effect of S on Superconductivity in $YBa_2Cu_3SO_{6-\delta}$

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In 1986, Bednorz and Muller found the superconductivity in the 30K range in $La-Ba-Cu-O$ compound.[1,2] Soon after this discovery, C. W. Chu and etc. announced their tremendous finding of superconductivity of 90-93K with a sharp transition region (1K) in $Y-Ba-Cu-O$ compound.[2] Scientists worldwide have much focused on searching new superconductors of higher transition temperature, T_c and the studies of physics and chemistries of these high T_c superconductors. The highest transition temperature T_c achieved so far is believed 125K in $Tl-Ca-Ba-Cu-O$ compounds.[3] Although, many models have been proposed to elucide the mechanism of the high T_c superconductivity in oxide compounds, no guidelines can really direct ones to enhance the superconductivity of existing high T_c superconductor or to invent the new superconductors. It seems that the empirical methods are still the way to approach these goals.

In the superconductors of oxides, oxygen atoms play a key role of the superconductivity[1]. From the x-ray and neutron diffraction[4] it was known that in the orthorhombic phase the oxygens are ordered along the $\underline{b}$ axis so as to form a one dimensional $Cu-O$ "chain" and a disordering of the oxygen vacancies along $\underline{a}$ axis. It is popularly agreed that the $Cu-O$ chains play an important role in the high T_c superconductivity. The lack of the isotope effect on the superconductivity in $Y-Ba-Cu-O$ compounds may suggest that the pairing mechanism is not a standard electron-phonon

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interaction[5]. According to Anderson (RVB) the hole amplitude drives true electron-pair amplitude via the hole-pair amplitude which has the same symmetry as a bound electron pair.[6] If so, a sufficient concentration of Cu^{+3} is required.[5] Varma et.al[5,7] proposed that the charge transfer exciton $Cu^{3+}O^{2-} \rightarrow Cu^{2+}O^{-}$ is the source of the effective electron-electron attraction.[5,7] And Mattheis et.al.[8] from their band structure calculations concluded that the superconducting properties of these oxides are mainly governed by the $Cu-3d$ and $O-2p$ electrons.[5] Chemical doping is one of the practical methods to confirm these proposed models, by knowing the precise locations of the impurities, and their ion structures. Much work has been focused on the doping of the Cu^{+} sites by positively charged ions, such as Zn^{+}, Ni^{+}, Fe^{+} and on Y^{+}, Ba^{+} sites by rare earth ions. Fewer studies on the effects of the substitution for O^{-} sites have been conducted. Our paper is in attempt devoted to the study of the change of the physical properties when S^{-} ions substitutes for O^{-} ions in $Y-Ba-Cu-O$ compounds.

Experiment Results

Sample preparation: Several $Y-Ba-Cu-S(O)$ samples have been synthesized by means of the use of different chemical components and heat treatments. Some samples were made from the mixture of Y_2O_3, $BaCO_3$, CuS and CuO, and some from the mixture of Y_2O_3, $BaCO_3$, $CuSO_4$ and CuO. The original oxides sulphide or sulphates were dried in a hot vacuum. According to the stoichiometric of the final compound $YBa_2Cu_3SO_6$. The appropriate amount of components were weighed and ground and mixed thoroughly. The powder is then pressed into pellets. The pellets are subject to two heat treatment processes: (a) samples were heated in air at 950°C for 24 hours or longer and cooled to room temperature in air, then ground, pressed into pellets again and (b) sintered in a furnace with O_2 flowing. The furnace temperature increases from room temperature to 950°C within five (5) hours, and stays at 95O°C for 16 hours, cools down to 500°C within five (5) hours, stays at 500°C for 16 hours and finally cools down

to room temperature within five (5) hours. The heat treatments processes may differ from sample to sample. The samples and their heat treatments processes are listed below:

> **Sample 1:** Components used are: Y_2O_3, $BaCO_3$, CuS, and CuO; and heat treatment, processes are: (a) once then process (b) twice.
>
> **Sample 2:** Components used are: Y_2O_3, $BaCO_3$, CuS, and CuO; heat treatment processes (a) once, then processes are: (b) three (3) times.
>
> **Sample 3:** Components used are: Y_2O_3, $BaCO_3$, $CuSO_4$, and CuO; and heat treatment processes are: (a) twice then process (b) once.

The electrical resistance measurements were carried out by means of standard four-probe technique with indian soldering points on the samples of rectangular bars of about 10 x 2 x 1 mm^3 cut from pellets. The data acquisitions were accomplished by Keithley's instruments and HP computer system. *Fig. 1 and Fig. 2* show the temperature-dependence of the resistivity of sample 1 and sample 2. In the temperature range from 300K down to liquid heliumm temperature the resistances of sample 1 and sample 2 were performed. From the electrical resistance point of view, before the superconductivity transition temperature sample 1 exhibits, insulator like electrical property. Shown in Fig. 1, the resistance increases when the temperature decreases. The onset temperature is about 94K. The zero resistance temperature is about 30K. Therefore, the transition region is wide. For sample 2, shown in Fig. 2, the resistance decreases monotonously as the temperature decreases. The onset temperature is also about 94K and transition region is very narrow, about three (3) or four (4) degrees. The "zero-R" state is at about 90K. The susceptibility measurements for those three (3) samples have been carried out at Quantum Design Sample Property Measurement System. Fig. 3 shows the temperature-dependence of susceptibility at magnetic strength of 2000g for sample 1. The embeded is the data of susceptibility of this sample

from 400K to the temperature before transition temperature and the solid curve is the best fit by Curie-like law $\chi = \chi_0 + \frac{c}{T+T^*}$ Meissner effect starts at the temperature around 91k. Fig. 4 shows the temperature-dependence of susceptibility at magnetic strength of 2000g for sample 2. The embedded graph is the data of susceptibility of sample 2 vs. temperate from 400K down to temperature before the transition temperature and the solid curve is the best fit by curie-like law. Fig. 5 is the similar plot for sample 3. From Fig. 3 (sample 1) it is obvious that the Meissner effect starts at about 90K, at 77K the susceptibility is about -0.04 (emu/mol), and the curie-like parameters are: $\chi_0 = 2.17 \, x \, 10^{-4}$ emu/mol, $C = 9.29 \, x \, 10^{-3}$ emu/mol, $T^* = 51.4K$ and magnetic moment $\mu_p = .273\mu_B$. For sample 2 from Fig. 4 the transition (Meissner effect takes place) is sharp at about 90K. At 77K the susceptibility is about 0.09 (emu/mol) which is almost double the value of sample 1 (0.04), and the curie-like parameters are : μ_0 = 4.78 x 10^{-4} emu/mol, c = 0.08 emu/mol. T^* = 17.7K, and the magnetic moment μ_p = .798 μ_B. For sample 3, the resistance measurement hasn't been done yet. However, the d.c. susceptibility measurement shows Meissner effect also, it seems that at temperature around 75K, the susceptibility becomes negative and the transition is broadened. The curie-like parameters are: χ_0 = 3.549 x 10^{-4} emu/mole, c = 5.34 x 10^{-2} emu/mole, T^* = 8.2K and magnetic moment μ_p =.654 μ_B. From the observations reported about, we may conclude that the transition temperatures T_c are not strongly affected by the impurity S that is in agreement with the prediction by non-BCS theory[9]. Whereas, the other models responsible for the high T_c superconductivity somewhat involve the electronic structure of the compound $YBa_2Cu_3SO_6$. For instance, the charge-transfer excitations would enable us to expect three d-d transitions, and the lowest one would be the $3d(3z^2 - r^2)$ to $3d(x^2 - y^2)$ excitation within the e_g orbitals[10]. The substitution of S for O may lead to some variations in the electrical and magnetic properties of YBa_2CuO_7. The susceptibility studies of YBa_2CuSO_6 do show the effects of S in the compound[9].

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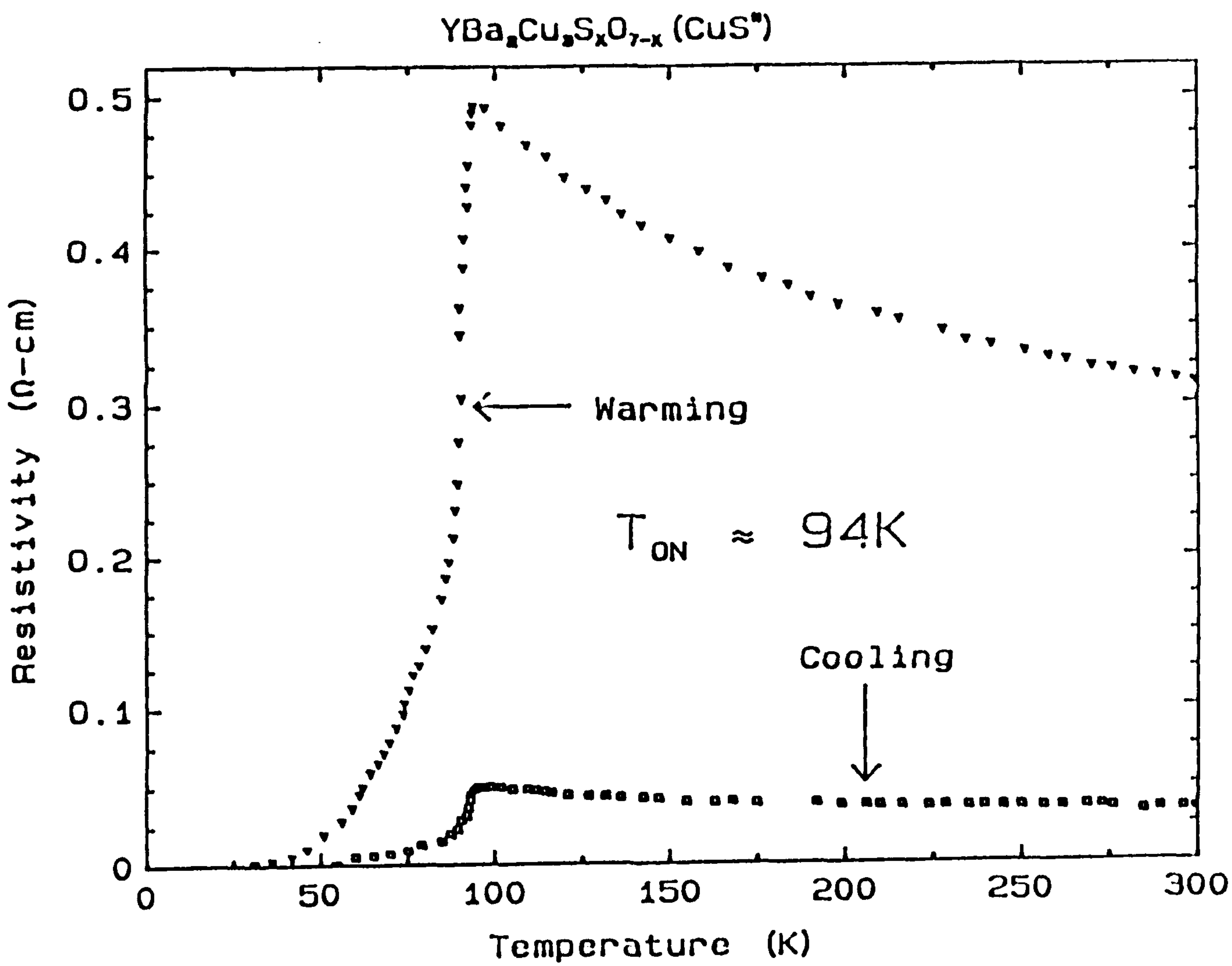
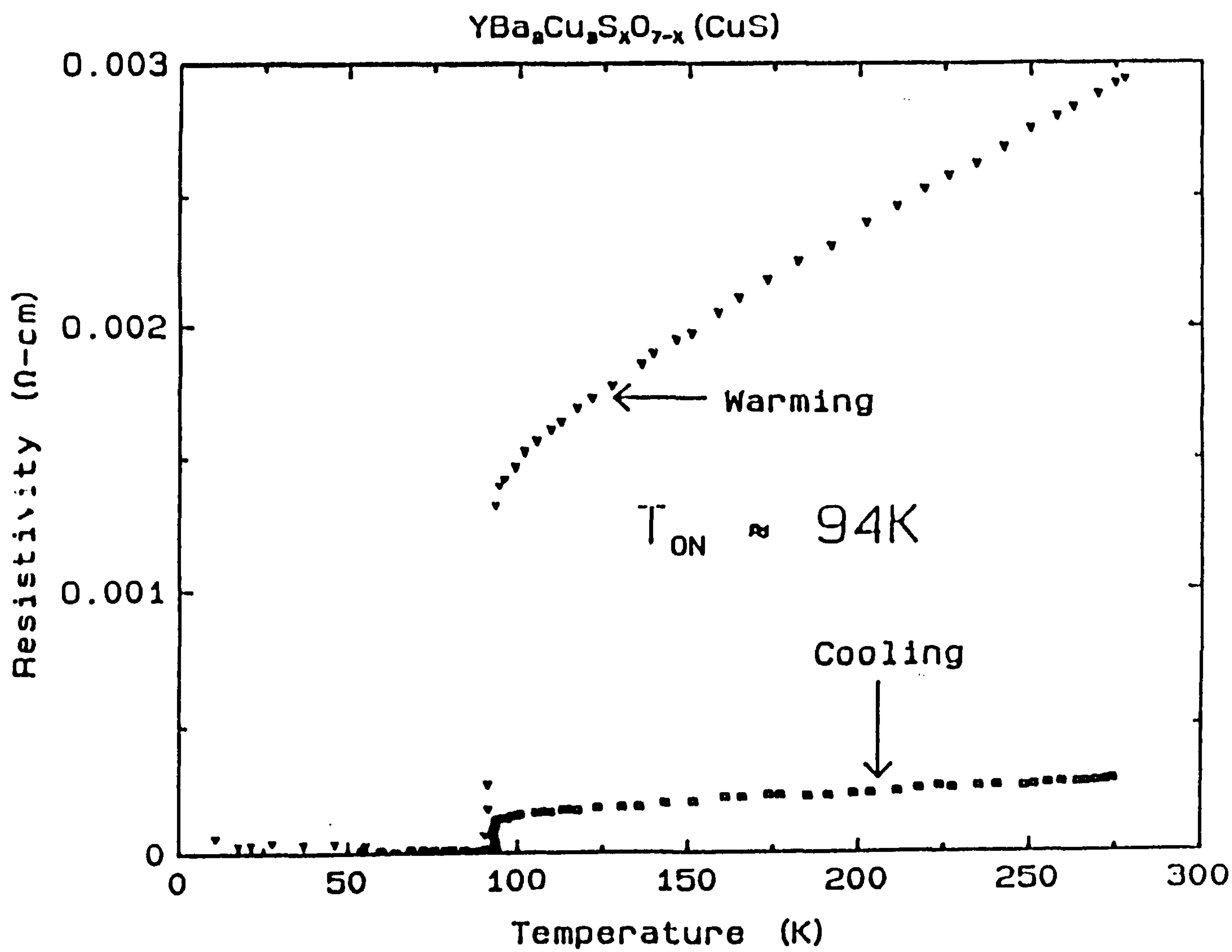

YBa2Cu3SxO7-x (CuS")
Resistivity (Ω-cm)
0.5
0.4
0.3
0.2
0.1
0
50
100
150
200
250
300
Temperature (K)
Warming
TON ≈ 94K
Cooling

FIGURE 1.



YBa2Cu3SxO7-x (CuS)
0.003
0.002
0.001
0
Resistivity (Ω-cm)
0
50
100
150
200
250
300
Temperature (K)
Warming
T_ON ≈ 94K
Cooling

FIGURE 2.

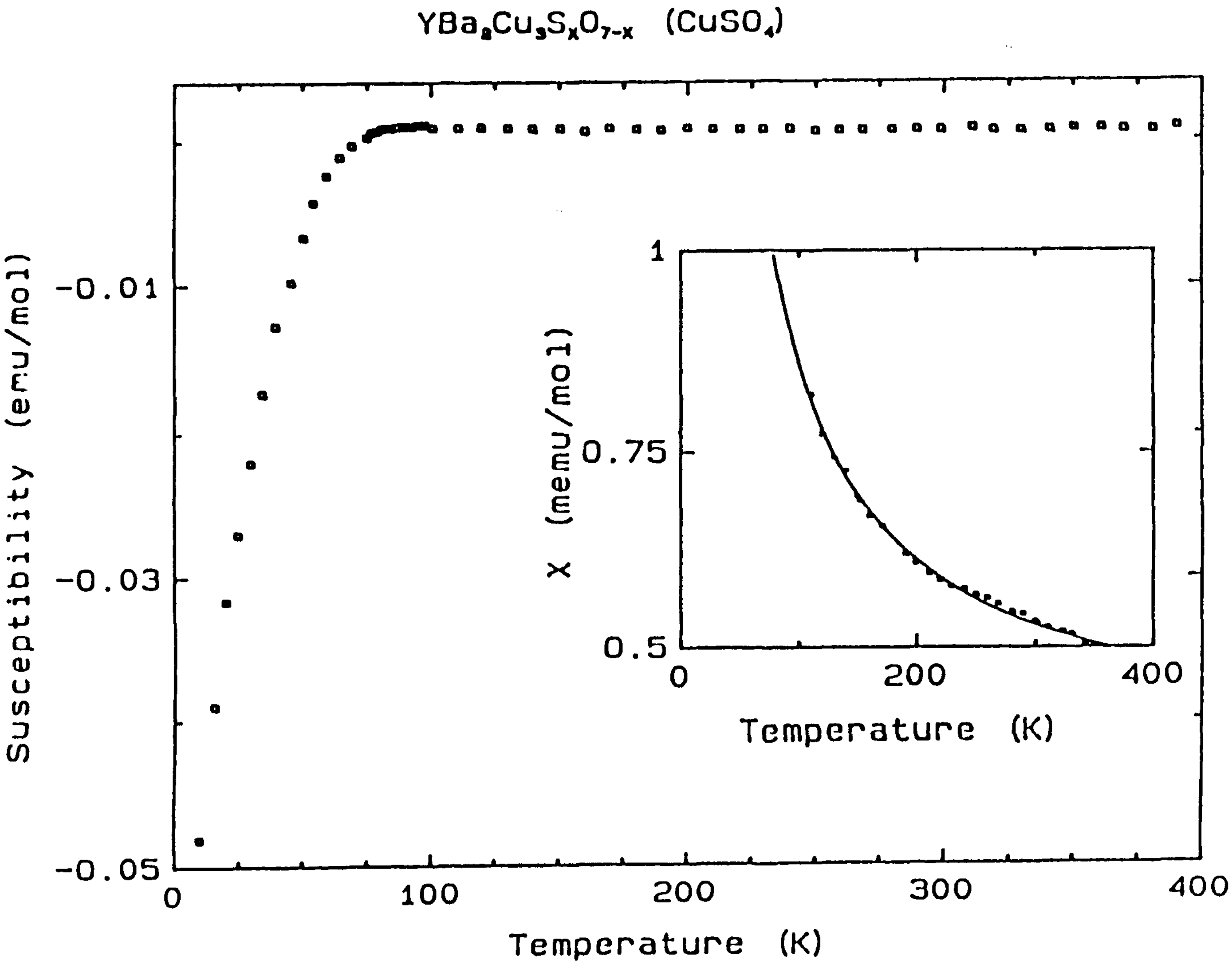
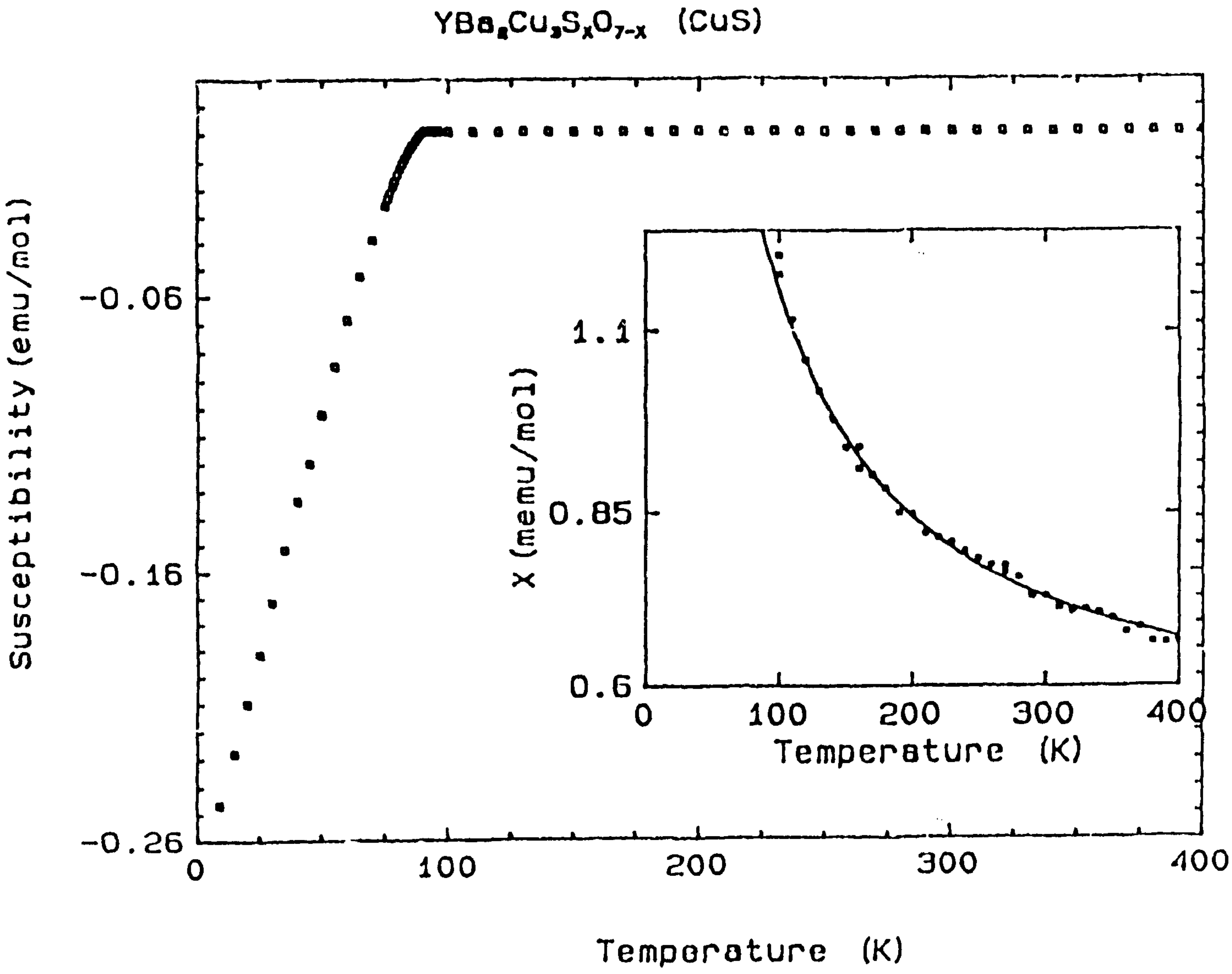
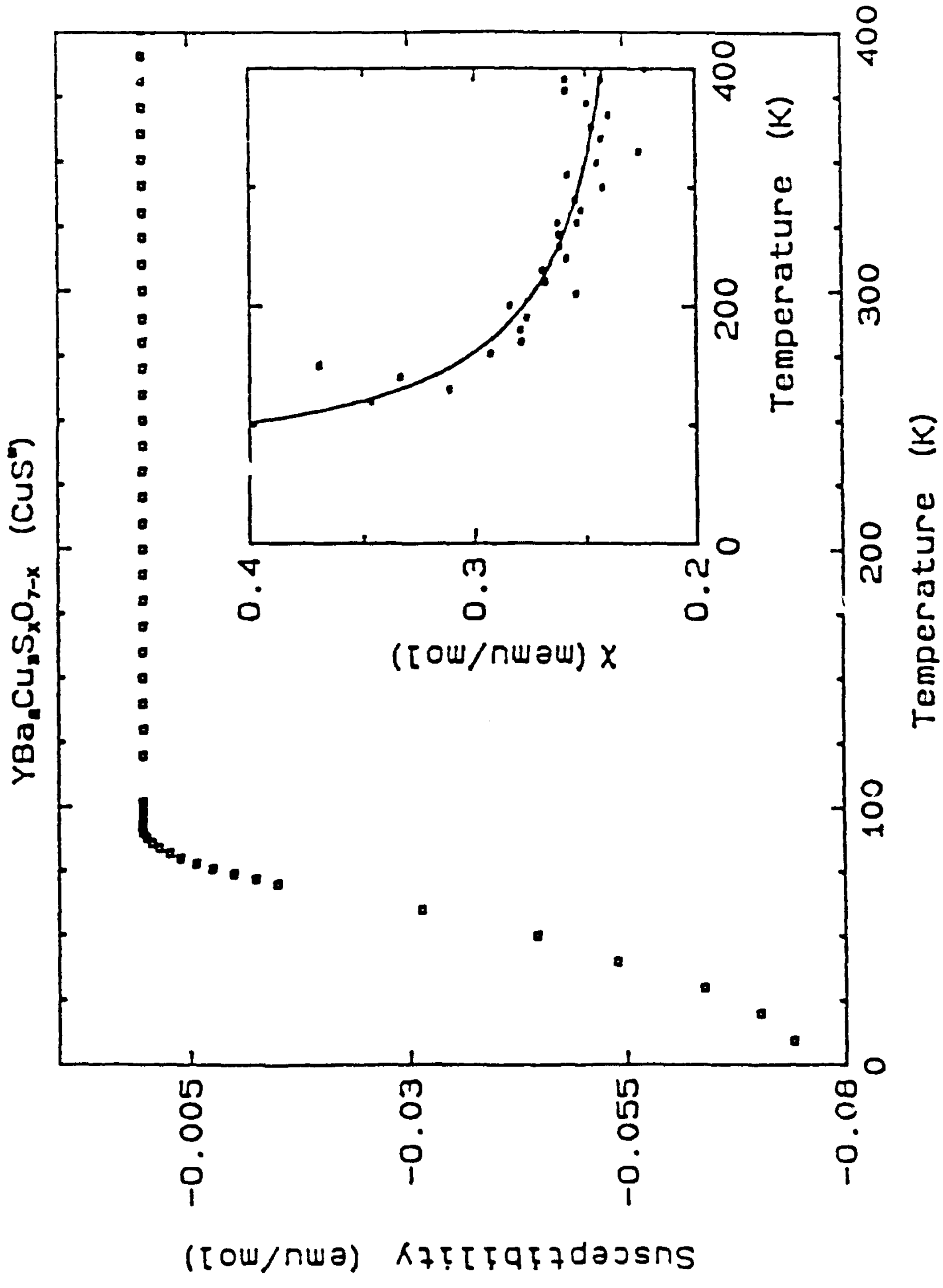

YBa$_2$Cu$_3$S$_x$O$_{7-x}$ (CuSO$_4$)
Susceptibility (emu/mol)
-0.01
-0.03
-0.05
0
100
200
300
400
Temperature (K)
X (memu/mol)
1
0.75
0.5
0
200
400
Temperature (K)

FIGURE 3.



YBa2Cu3SxO7-x (CuS)
Susceptibility (emu/mol)
-0.06
-0.16
-0.26
0
100
200
300
400
Temperature (K)
X (memu/mol)
1.1
0.85
0.6
0
100
200
300
400
Temperature (K)

FIGURE 4.



YBa2Cu3SxO7-x (CuS*)
Susceptibility (emu/mol)
-0.005
-0.03
-0.055
-0.08
0
100
200
300
400
Temperature (K)
χ (memu/mol)
0.4
0.3
0.2
0
200
400
Temperature (K)

FIGURE 5.